ABSTRACTS

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THE APPLICATION OF NMR SPECTROSCOPY TO THE STUDY OF PLATINUM AND PLATINUM GROUP COMPOUNDS

BRIAN E. MANN

The paper will consist of two parts. Firstly, the use of NMR spectroscopy to study platinum complexes will be reviewed, and then recent results from my own research will be discussed.

The use of ^{1}H, ^{13}C, ^{15}N, ^{31}P, and ^{195}Pt NMR spectroscopy to examine platinum complexes will be examined. The role of techniques such as NOE, COSY, INEPT, DEPT $^{13}C\{^{1}H\}$ correlation, and inverse detection will be discussed.

Extensive use has been made of NMR spectroscopy to detect reaction intermediates. Recently this has been particularly successful for the hydrogenation catalyst, $[RuCl(H)(PPh_3)_3]$. We have already shown that $[RuCl(H)(PPh_3)_3]$ reacts with cyclohepta-1,3-diene to give $[(\eta^3 - C_7H_{11})RuCl(PPh_3)_2]$ and then $[(\eta^5 - C_7H_9)RuCl(PPh_3)_2]$[1,2]. Further investigation of $[(\eta^5 C_7H_9)RuCl(PPh_3)_2]$ shows that it undergoes dissociative PPh_3 exchange, even at $-30°C$, to give the highly reactive $[(\eta^5 - C_7H_9)RuCl(PPh_3)]$. Treatment of $[(\eta^5 - C_7H_9)RuCl(PPh_3)_2]$ with H_2 yields first $[(\eta^3 - C_7H_{11})RuCl(PPh_3)_2]$ and then $[Ru_2H_4Cl_2(PPh_3)_4]$,

which always contains some $[RuCl(H)(PPh_3)_3]$. This solution is a more powerful hydrogenation catalyst than $[RuCl(H)(PPh_3)_3]$. Alternatively, $[RuCl(H)(PPh_3)_3]$ can be produced by adding one equivalent of PPh_3 to $[(\eta^5 - C_7H_9)RuCl(PPh_3)_2]$ before hydrogenation. As solid $[(\eta^5 - C_7H_9)RuCl(PPh_3)_2]$ is indefinitely stable in air, it provides a convenient precursor for the $[RuCl(H)(PPh_3)_3]$ hydrogenation catalyst.[3]

The mechanism of carbonyl scrambling in $[Ir_4(CO)_{11}L]$, $L = PEt_3$, PH_2Ph, and $PHPh_2$ has been investigated using magnetization transfer measurements. It is shown that there are two main mechanisms operating, and there is a substantial barrier separating the bridged and unbridged intermediates.[4,5]

The trigonal twist mechanism has been demonstrated in $[RuH_2(CO)(PPh_3)]$ using EXSY.[6] It will be shown how exchange between lines of multiplets yields specific information on chemical exchange mechanisms.

REFERENCES

[1] Grassi M., Mann B.E., Manning P., Spencer C.M., *J. Organomet. Chem.*, **1986**, 307, C55-C57.

[2] Alibrandi G., Mann B.E., *J. Chem. Soc., Dalton Trans.*, in press (April 1994).

[3] Sun G. A., unpublished work.

[4] Mann B. E., Pickup B.T., Smith A.K., *J. Chem. Soc., Dalton Trans.*, **1989**, 889.

[5] Mann B. E., Vargas M.D., Khattar R., *J. Chem. Soc., Dalton Trans.*, **1992**, 1725.

[6] Ball G.E., Mann B. E., *J. Chem. Soc., Chem. Commun.*, **1992**, 561.

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X-RAY AND NEUTRON SCATTERING STUDIES OF $Pt - H$ INTERACTIONS

A. ALBINATI

The study of the nature of the $M - H$ and $M - H - M'$ interactions has been an active area of research for a long time.

One of the most interesting aspect of this study has been the relationship between molecular architecture and bonding. While many polyhydrido complexes have been described, some features observed in mono-hydrido bridged systems show that these are worthy of a detailed study as they may provide a better insight into the nature of the $M - H - M$ bond.

A class of compounds suitable for this type of study is shown below:

$$\begin{array}{ccc} PR_3 & PR_3 & + \\ | & | & \\ L - Pt - H - Pt - L' & & \\ | & | & \\ PR_3 & PR_3 & \end{array}$$

$L = L' = C_6H_5, C_6F_5, H$; $L = C_6H_5$, $L' = H$; $R = PMe_3, PEt_3$.

In this series of complexes (1) systematic variations of L and L' migth allow to establish the influence of electronic factors on their structures. Thus X-ray structural studies have been carried out on some members of this series, but, given the well known limitations of the X-ray data, more informations were needed for a complete characterization (e.g. accurate values for the $M - H - M$ angle). As it proved impossible to obtain crystals suitable for neutron diffraction, an Incoherent Inelastic Neutron Scattering ($IINS$) study was carried out to obtain a detailed picture of $M - H$ vibrations (2). The $IINS$ data toghether with those from diffraction lead to a satisfactory description of these hydrides.

A second type of $M - H$ interaction appears when a transition metal is proximate to a carbon-hydrogen bond leading to the formation of a $M \cdots H - C$ "moiety". The strength of this interaction may vary from the strong "*agostic*" case (a 2e-3c bond) (3) to the weak "*remote*" as found in complexes like *trans*-$LPtCl_2$ (quinoline-8-carbaldehyde) (4).

We have developed criteria, both in the solid state (structural parameters) and in solution ($J(Pt, H)$) to recognize these interactions and define the geometric and electronic factors necessary for their existence. Thus it is possible to "*tune*" these interactions by an appropriate choice of the ligand X (5).

Some of the recent results obtained by this approach will be discussed.

REFERENCES

[1] Carmona D., Thouvenot R., Venanzi L.M., Zambonelli L., *J. Organomet Chem.*, **1983**, *250*, 589.

[2] Albinati A., Eckert J., Hofmann P., Ruegger H., Venanzi L.M., *Inorg. Chem.*, **1993**, *32*, 2377.

[3] Brookhart M., Green L.M.H. *J. Organomet. Chem.*, **1983**, *250*, 395.

[4] Albinati A., Pregosin P.S., Wombacher F., *Inorg. Chem.*, **1990**, *29*, 1812.

[5] Albinati A., Lianza F., Pregosin P.S., Mueller B., *Inorg. Chem* in press.

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LUMINESCENCE PROPERTIES OF PLATINUM(II) COMPLEXES

SEBASTIANO CAMPAGNA

Excited state properties of transition metal complexes, in particular luminescence, are extensively studied because of both fundamental and applicative reasons. Solar energy conversion and information storage and treatment are research fields which are profoundly based on photoinduced energy and electron transfer processes involving metal complexes. While many efforts in transition metal photochemistry and photophysics have been devoted to d^6 metals such as $Ru(II)$ and $Os(II)$, the excited state properties of $Pt(II)$ complexes have been investigated only at a minor extent.

Here the requirements for designing luminescent $Pt(II)$ complexes are briefly discussed, along with some representative examples of known luminescent $Pt(II)$ complexes. The compounds are adducts of $[Pt(bpy)(NH_3)_2]^{2+}$ with crown ethers, Pt-cyclometallated species, and $[Pt(LL)(X)_2]$ systems ($bpy = 2,2'$-bipyridine; LL=chelating polypyridine species; X= halides, CN).

Investigations on two new classes of luminescent $Pt(II)$ complexes recently synthesized in our department are also

reported. The first class of compounds includes tight contact ion pairs of general formula $\{Pt(R_2 - DTO)_2^{2+}, (X^-)_2\}$ (DTO=protonated dithiooxamide; R=benzyl, n-butyl, methyl, cyclohexyl; $X = Cl, Br, I$). These species exhibit room temperature luminescence with lifetimes in the nanosecond time scale, originating from σ-bond $Pt(d\pi)/S(p)$-to-π^* (dithiooxamide) charge transfer ($SBLCT$) excited state (s). The second class of complexes includes $[Pt(R - terpy)X]^+$ and $[Pt(R\text{-terpy})Cl]^+$ complexes ($R = H, Ph$; $X = CH_3, Ph$). They exhibit 77 K long-lived (microsecond time scale) luminescence from ligand-centered (LC), $Pt(d\pi)$-to-terpy(π^*) charge transfer ($MLCT$) and/or $Pt - Pt(d\sigma^*)$-to-terpy(π^*) charge transfer (Pt_2-to-terpy) levels. $Pt - Pt(d\sigma^*)$ orbitals are formed from the antibonding interaction between dz^2 orbitals of two $Pt(II)$ metal ions. Coupling origins from intermolecular interactions of head-to-tail stacked molecules. (Pt_2-to-terpy) luminescence can here be regarded as a probe of the stacking interaction.

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METAL-METAL BONDS IN FIVE-COORDINATE PLATINUM(II) COMPLEXES

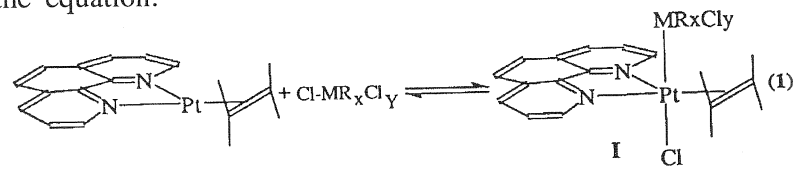
ACHILLE PANUNZI

It is well known that the catalytic properties of transition ions can be enhanced by the presence of a main group metal in their coordination sphere [1].

For example, complexes containing $Pt(II) - E$ bonds $(E = Ge, Sn, Pb)$ catalyze the hydroformylation, isomerization and hydrogenation of unsaturated compounds [1,2]. The intermediates occurring in these processes are tipically five coordinate platinum(II) species containing the metal atom and the olefin in *cis* position. In spite of this, scant examples of stable complexes containing similar coordination environments have been described.

On these grounds and taking into accounts the well-known properties of sterically hindered bidentate ligands, which markedly stabilize trigonal bipyramidal arrangement around d^8 ions [3], we have developed [4] the synthesis of five-coordinate olefin platinum(II) complexes containing an organometal fragment in axial position. The binuclear species have been synthesized through oxidative addition of organometal halides to three-coordinate platinum(0) precursors, according to

the equation:



$M = Ge, Sn, Pb; x + y = 3$

$M = Hg; x = 1, y = 0.$

In addition to the interest for the unusual coordination number, type **I** complexes deserve attention at least in two further respects:

i) in the case of organomercury and organotin halides, reaction (1) is an equilibrium and represents a rare example of reversible oxidative addition process in the chemistry of platinum(0).

ii) the coordinative saturation of platinum atom greatly enhances the stability of organometal fragments, such as $Pt - PbR_2Cl$ and $Pt - HgR$, which commonly undergo fast decomposition processes [5].

REFERENCES

[1] See for example: M.S. Holt, W.L. Wilson, J.H. Nelson, *Chem. Rev., 89* **(1989)** 11.

[2] H. A. Tayim, J.C. Bailar Jr., *J. Am. Chem. Soc., 89* **(1967)** 3420 and ref. therein.

[3] V. G. Albano, G. Natile, A. Panunzi, *Coord Chem. Rev.,* in print.

[4] F. Ruffo, *Tesi di Dottorato in Scienze Chimiche (Vl Ciclo),* Università di Napoli, and ref. therein.

[5] V.I. Sokolov, V.V. Bashilov, 0.A. Reutov, *J. Organomet. Chem., 97* **(1975)** 299.

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HETEROMETALLIC PLATINUM CARBONYL CLUSTERS: SYNTHETIC STRATEGIES AND MOLECULAR GEOMETRIES

A. CERIOTTI

Heterometallic carbonyl clusters are helpful models for the metallic state and for the stereochemical implications concerning the chemi- and physisorption of carbon monoxide into metal surfaces. [1] However, a prerogative of a molecular metal cluster, strictly related to the presence of ligands, is the possibility of adopting different metal packings, no matter what metal packing is adopted in bulk, and, at the same time, of showing unusual structure forbidden in bulk. Thus, the occurrence of a particular metal polyhedron in heterometallic carbonyl clusters is probably due to a delicate balance between electronic needs of different metals, internal and external steric factors and crystal lattice requirements.

The present lecture will focus mainly on high-nuclearity carbonyl metal clusters containing platinum, an electron-rich metal with a relatively high atomisation energy, which is able to support and stabilize large metal skeletons with relatively few carbon monoxide ligands. As a matter of fact, due to the progressive flattening of the polyhedral surfaces, the steric

requirements of the ligands increase exponentially with the cluster size.[2]

In this lecture, the synthetic strategies (thermal activation, oxidative condensation or coupling, reductive carbonylation and redox condensation, etc.) and the molecular geometries (polyhedra as bulk metal fragments, condensed polyhedra, etc.) of the more significant high-nuclearity heterometallic platinum carbonyl clusters will be systematically presented by giving an overview of the already known $Pt-Rh$, $Pt-Ni$ and $Pt-Os$ systems [3] and presenting more recent results on the synthesis and characterization of new large carbonyl metal clusters belonging to the $Pt-Ru$ system, viz. $[Ru_9Pt_6(CO)_{28}]^{4-}$ and $[Ru_6Pt_3H_2(CO)_{21}]^{2-}$. The molecular structures of the above $Pt-Ru$ anionic clusters are nice examples of polyhedra as bulk metal fragments (b.c.c.), as in $[Ru_9Pt_6(CO)_{28}]^{4-}$ and of condensed polyhedra (face sharing octahedra), as in $[Ru_6Pt_3H_2(CO)_{21}]^{2-}$. Very recent results on the $Pt-Sn$ system will be also presented and discussed. Such a system is extremely important for its potential implication in the catalytic hydroformylation. The $[Pt_8(SnCl_2)_4(CO)_{10}]^{2-}$ and $[Pt_6(SnCl_2)_2(SnCl_3)_4(CO)_6]^{4-}$ anionic clusters have been prepared by reacting a Pt carbonyl cluster, belonging to the series of inorganic oligomers $[Pt_3(CO)_6]_n^{2-}$ $(n=3,4,5)$, with $SnCl_2$. The purpose of this chemistry was to cheek the behaviour of a molecular metal cluster with an electrophile and to test whether the site of interaction could be the softer part of the cluster, e.g. the metal core, or the harder part represented by the oxygen atoms of the carbonyl groups. The above $Pt-Sn$ anions have been completely characterized by x-ray analysis. The molecular structure of $[Pt_8(SnCl_2)_4(CO)_{10}]^{2-}$ can be described as a cluster-adduct deriving from the condensation of three edge-sharing tetrahedra of Pt atoms bearing intact $SnCl_2$ into external "butterfly"surfaces. Instead, in the $[Pt_6(SnCl_2)_2(SnCl_3)_4(CO)_6]^{4-}$ anionic cluster

two edge-sharing tetrahedra of Pt atoms, forming the metallic skeleton, bear two $SnCl_2$ moieties and four additional $SnCl_3^-$ groups as edge- face-bridging ligands.

REFERENCES

[1] J.D. Roth, G.J. Lewis, L.K. Safford, X. Jiang, L.F. Dahl, M.J. Weaver, *J. Am. Chem. Soc., 114*, (**1992**) 6159.

[2] P. Chini, *Gazz. Chim. It., 109,* (**1979**) 225.

[3] A. Ceriotti, R. Della Pergola, L. Garlaschelli, in *Physics and Chemistry of Metal Cluster Compounds, Dordrecht Kluwer,* in the press.

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CURRENT STATUS OF STRUCTURE-ACTIVITY RELATIONSHIPS OF PLATINUM ANTITUMOR AGENTS. COMPLEXES ACTING BY NON-CLASSICAL MECHANISMS

NICHOLAS FARRELL

Direct structural analogs of the anticancer drug *cis*-$[PtCl_2(NH_3)_2]$ (*cis*-DDP) in clinical trials have not shown significant improvement over the parent drug. A possible mechanistic explanation for this finding is that all analogs produce a very similar array of adducts to those of *cis*-DDP. Our group has explored the possibility that alteration of the mode of DNA binding of Pt complexes in comparison to *cis*-DDP may result in a different spectrum of antitumor activity. Two sets of complexes are currently under study - dinuclear "bisplatinum" complexes and the series *trans*-$[PtCl_2(L)(L')]$ ($L = L' =$ pyridine, $L = NH_3$, $L' =$ pyridine, thiazole and quinoline). This contribution summarises our chemical and biological studies on these new antitumor agents, which violate the empirical structure-activity relationships. Supported by American Cancer Society and Boehringer Mannheim Italy.

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ASPETTI DELLA REATTIVITÀ DI COMPLESSI DI PLATINO, DI POTENZIALE INTERESSE BIOMEDICO, CON LEGANTI ALLO ZOLFO

A. PASINI - M. LUPATINI - P. PEREGO

Verrà presentata e discussa la reattività di complessi di platino(II) del tipo $[Pt(en)L]^+$ (dove en = etilendiammina e L sono una serie di chelanti i cui atomi donatori sono ossigeno e zolfo di solfossidi e tioeteri), verso lo ione Cl^- e 5′-GMP. Questi nucleofili reagiscono sostituendo gli atomi donatori O e/o S con modalità che dipendono dalla natura del ciclo chelante e dell'atomo di zolfo (solfossido *vs* solfuro). La GMP si è mostrata più reattiva dello ione cloruro e, come atteso, il legame Pt-S dei tioeteri risulta essere più stabile/inerte di quello dei solfossidi. Alcuni intermedi di reazione del tipo [Pt(en)(Cl)L] e [Pt(en)(GMP)L] (con L monodentato e coordinato al Pt tramite lo zolfo) sono risultati così stabili da poter essere isolati e caratterizzati.

La citotossicità dei complessi $[Pt(en)L]^+$ (che è risultata essere abbastanza bassa) non sembra essere correlabile con la loro reattività.

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INTERSTRAND DNA ADDUCTS OF PLATINUM COMPLEXES

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Numerous studies suggest that the antitumor action of platinum drugs is related to its ability to react with cellular DNA. The platinum drugs bind to DNA preferentially to guanine residues at the N(7) position, producing monofunctional adducts that can subsequently close to bifunctional lesions. Most of the structural information currently available pertains to the intrastrand cross-links of platinum between adjacent purines. 90% of these adducts are formed in the reaction of linear double stranded DNA with *cis*-diaminedichloroplatinum (II) (cisplatin), which is one of the most effective anticancer drugs. Its minor DNA adducts are monofunctional lesions, interstrand cross-links and intrastrand cross-links between two nonadjacent purines.

Clinically ineffective *trans* isomer of cisplatin (transplatin) cannot form intrastrand cross-links between adjacent purines for sterical reasons. It has been, therefore, speculated that these DNA adducts of clinically effective cisplatin and its simple analogues are most likely responsible for antitumor activity of these drugs. Nevertheless, the DNA lesion (or lesions) of cisplatin and its simple analogues related to antitumor effect of platinum complexes still remains (or remain) to be established conclusively.

The bifunctional platinum complexes can form DNA interstrand crosslinks, but these lesions are not considered the lesions responsible for antitumor effect. This view is mainly derived from the observation that clinically ineffective transplatin forms more interstrand cross-links than does cisplatin. The latter speculation is, however, based on the assumption that both isomers form identical interstrand DNA lesions. However, DNA interstrand cross-links of transplatin have been studie less thoroughly so that the latter assumption has no experimental support.

A systematic study of the interstrand lesion formed in DNA by clinically ineffective transplatin revealed that this lesion was formed between the sites in DNA, which were different from those involved in the interstrand cross-link of cisplatin. In addition, the DNA interstrand cross-links of cisplatin and transplatin induce in DNA different conformational alterations.

In addition, we have found that the amount of interstrand cross-links formed by cisplatin or transplatin in supercoiled DNA is markedly higher in comparison with the amount of these lesions formed in linear or relaxed DNA. The effect increased with the decreasing level of the platination. Interestingly, the modification of negatively supercoiled DNA corresponding to 1 platinum bound per 5×10^5 nucleotide residues resulted mainly in interstrand cross-links so that this lesion became a major DNA adduct.

Taken together, the results of this work support the view that the role of the DNA interstrand lesions in the mechanism of antitumor effect of platinum drugs is significant, so that it deserves further examinations.

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STEREOSPECIFIC HYDROGEN BONDING IN PLATINUM NUCLEOTIDE INTERACTIONS

GIOVANNI NATILE

In DNA *cis*-DDP cross-links adjacent purine residues in a Head-to-Head (HH) conformation in which both the H8 atoms are on the same side of the platinum coordination plane. When the two nucleotide moieties are not linked by a phosphodiester group, the purines can have orientations in which the H8s are on opposite sides of the platinum coordination plane; this orientation is designated Head-to-Tail (HT) [1]. Normally only HT complexes are detected in solution and in most solid state crystallographic studies [2, 3]. The HH atropisomer, which is the best model for intrastrand binding of *cis*-platinum compounds to DNA, is difficult to isolate and has been found only in a crystal structure of *cis*-$[Pt(NH_3)_2(9\text{-ethyl-guanine})_2]X_2$ [4].

Investigation of complexes of the type $[Pt(5'GMP)_2(R, S, S, R\text{-}Me_2DAB)]$ (Me_2DAB=N,N′-dimethyl-2,3-diaminobutane and the configurations at the four asymmetric centres are R, S, S, and R at N, C, C, and N, respectively) has led to the first evidence for the existence of a HH atropisomer in solution [5]. In addition, the HH atropisomer is found to exist in equilibrium with two HT atropisomers, the predominant HT

having the Λ conformation. This is the first determination of the chirality of a HT species in solution; the ΔHT conformation had been found in all documented solid state structures for 6-oxopurine nucleot(s)ide complexes with metal centres [3].

The favoured HT atropisomer can form two O6-NH H-bonds, the HH atropisomer can form one O6-NH H-bond and the other HT atropisomer cannot form any O6-NH H-bond. Thus, O6-NH H-bond appears to dominate the stereochemistry of these complexes. For the complex with all asymmetric centres on Me_2DAB inverted, [Pt(5′GMP)$_2$(*S*, *R*, *R*, *S*-Me_2DAB)], the dominant atropisomer has the ΔHT configuration. This result demonstrates that the stereochemistry of the ammine ligand influences the conformational equilibrium between atropisomers. The use of platinum(ll) complexes of stereochemically controlling ligands shows promise for controlling DNA or RNA conformations.

A similar investigation performed on the less symmetrical [Pt(5′GMP)$_2$-(*S*, *R*, *R*, *R*-Me_2DAB)] and [Pt(5′GMP)$_2$(*S*, *S*, *S*, *R*-Me_2DAB)] species has also demonstrated that both O6-NH and $ROPO_3$-NH H-bonds are important in determining the formed atropisomer [6].

The O6 can participate in H-bonding only when the O6 and the NH are on the same side of the coordination plane. When, instead, the H8 and the NH are on the same side, only phosphate group H-bonding is possible since in the normal anti conformation of 5′GMP, the phosphate group is close to H8 and hence to NH. Because the sugar moiety is flexible and there is relatively free rotation about the glycosyl bond, it is possible that a H-bond between the phosphate group and the NH is formed also when the H8 and NH are on opposite sides of the coordination plane. A quasi-equatorial NH is found to be particularly suitable to donate a strong hydrogen bond to the phosphate.

In conclusion modelling the stereochemistry of the NH atoms can lead to compounds with a strong preference for forming one type of adduct.

REFERENCES

[1] R. E. Cramer, P. L. Dahlstrom, *Inorg. Chem.* **24** (1985) 3420.

[2] M. D. Reily, L. G. Marzilli, *J. Am. Chem. Soc.* **108** (1986,) 6785.

[3] B. Lippert, Prog. *Inorg. Chem.* **37** (1989) 1.

[4] B. Lippert, G. Raudaschl-Sieber, C. J. L. Lock, P. Pilon, *Inorg. Chim. Acta,* **93** (1984) 43. G. Schöllhorn, G. Raudaschl-Sieber, G. Müller, U. Thewalt, B. Lippert, *J. Am. Chem. Soc.* **107** (1985) 5932.

[5] Y. Xu, G. Natile, F. P. Intini, L. G. Marzilli, J. Am. Chem. Soc. **112** (1990) 8177.

[6] D. Kiser, F. P. Intini, Y. Xu, G. Natile, L. G. Marzilli, unpublished work.

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AMINO ACIDS AND PEPTIDES Pt(II) COMPLEXES: STRUCTURE AND PROPERTY

V. PAVONE - A. LOMBARDI - M. SAVIANO - O. MAGLIO

Amino acids and peptides complexes of transition metal ions have been object of several studies during the last years and their preparation and properties have been recently reviewed.[1]

Much of the interest in this field arises since these complexes can be useful intermediates in peptide synthesis.

Platinum has been successful used protecting amino group of α-amino acids in peptide synthesis.[2] A series of reactions at the carboxylic group of N-coordinated α-amino acids has been carried out to give Platinum(II) complexes with peptide esters, α amino acids amides and anhydrides as ligands. These reactions have never been applied to highly hindered residues, such as the α-aminoisobutyric acid (α-methyl alanine or α, α' dimethyl glycine, Aib), that shows reduced reactivity and thus low reaction yields.

With the aim of investigating the effect of electron-withdrawing properties of the Pt(II) in increasing the reactivity of N-coordinated amino acid in the peptide bond formation, we have undertaken a systematic study on the reactivity of Pt(II) N-coordinated α-amino acids[3].

The condensation reactions of Pt(II)-amino acids complexes with sterically hindered residues, have been studied, and a detailed solid state X-ray analysis has also been carried out.

In Platinum(II)-peptide complexes we have observed marked effect on the conformation of the amino acidic N-coordinated residue.

REFERENCES

[1] W. Beck, B. Purucker and E. Srissel, *Chem. Ber., 106*, (**1973**), 1781.

[2] W. Beck, H. Bissinger, T. Castrillo de Castro, L. Olgemoller and B. Purucker, *Chem. Ber., 118*, (**1985**), 3135.

[3] A. Lombardi, O. Maglio, E. Benedetti, B. Di Blasio, M. Saviano, F. Nastri, C. Pedone and V. Pavone, Inorg. Chim. Acta, *196*, (**1992**), 241.

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SYNTHESIS AND REACTIVITY OF SOLVATED CATIONS OF PLATINUM(II)

LARS I. ELDING

Reactions of solvated homoleptic metal ions are fundamental for understanding of both complex formation reactions and many inner-sphere redox processes. Such complexes are also the natural starting materials for thermodynamic studies of complex formation and for synthetic coordination chemistry.

In the case of platinum(II), the tetraaqua cation was not prepared until 1976.[1] Since then, it has been used both as starting material for synthesis of other solvento complexes and for various reactivity studies.

A number of organic solvates, including those of the ambidentate dimethyl sulfoxide,[2] propionitrile,[3] and various monodentate and bidentate thioethers,[4] have been prepared and characterized both as solid compounds and in solution by use of EXAFS and LAXS.[5] The teraaqua cation itself has so far eluded all attempts at crystallizing in well-defined solid compounds.[6]

Since the first investigation of a square-planar solvent exchange in 1982,[7] a variety of such reactions have been studied.[8–11] In spite of the fact that those processes are chemically simple, reactivity comparisons are hampered, since

the contributions from the entering and leaving groups, *trans*- and *cis*-ligands, and stereochemistry are not separable.[12] This limitation also refers to activation volumes.[12] A comparison between analogous platinum(II) and palladium(II) exchange processes indicates that for exchange of strongly interacting ligands like olefins or carbon monoxide the two metal centers approach each other in reactivity.[13,14]

Kinetic studies of reversible complex formation reactions of solvento complexes of palladium and platinum indicate five-coordinate transition states with less orbital overlap, weaker and longer metal-ligand bonds, and less extensive solvation in the case of palladium(II).[12] This is in accord with the observed weaker *trans*-and entering ligand effects in substitution at palladium(II) centers compared to those of platinum(II).

REFERENCES

[1] Elding L. I., *Inorg. Chim. Acta* **1976**, 20, 65.

[2] Elding L. I., Oskarsson Å., *Inorg. Chim. Acta* **1987**, *130*, 209.

[3] Kukuskin V., Yu., Oskarsson Å., Elding L. I., *Inorg. Synth.*, **1993**, *31*, in press.

[4] Bugarcic Z., Norén B., Oskarsson Å., Stälhandske C., Elding L. I., *Acta Chem. Scand.* **1991**, *45*, 361.

[5] Hellquist B., Bengtsson L. A., Holmberg B., Hedman B., Persson I., Elding L. I., *Acta Chem. Scand.* **1991**, *45*, 449.

[6] Elding L. I., Oskarsson Å., *Inorg. Chim. Acta* **1985**, 103, 127.

[7] Gröning Ö., Drakenberg T., Elding L. I., *Inorg. Chem.* **1982**, *21*, 1820.

[8] Helm L., Elding L. I., Merbach A. E., *Inorg. Chem.* **1985**, *24*, 1719.

[9] Ducommon Y., Helm L., Merbach A. E., Hellquist B., Elding L. I., *Inorg. Chem.* **1989**, *28*, 377.

[10] Gröning Ö., Elding L. I., *Inorg. Chem.* **1989**, 28, 3366.

[11] Frey U., Elmroth S., Moullet B., Elding L. I., Merbach A. E., *Inorg. Chem.* **1991**, *30*, 5033.

[12] Elmroth S., Bugarcic Z., Elding L. I., *Inorg. Chem.* **1992**, 31, 3551.

[13] Olsson A., Kofod P., *Inorg. Chem.* **1992**, *31*, 183.

[14] Olsson A., Roodt A., Bojczuk M., Heaton B., Elding L. I., *J. Chem. Soc. Dalt.* **1992**, *to be submitted.*

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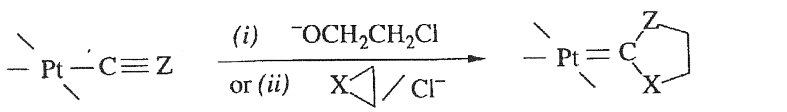
CYCLOADDITION AND COUPLING REACTIONS OF PLATINUM-COORDINATED LIGANDS. STOICHIOMETRIC AND CATALYTIC SYNTHESES OF HETEROCYCLES AND CYCLOPROPANES

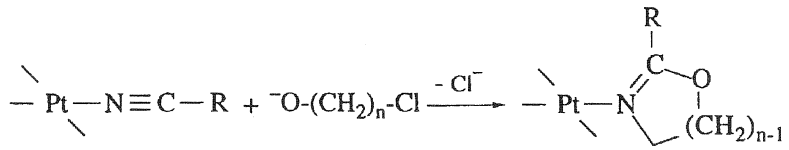
U. BELLUCO - R. BERTANI - G. FACCHIN
R. A. MICHELIN - M. MOZZON - L. ZANOTTO

$Pt(II)$-coordinated isocyanide and carbonyl ligands can be converted to 5- or 6-membered heterocyclic carbenes by reactions with a new class of organic nucleophiles such as haloalcohols, haloamines and the three-membered heterocycles $\overline{XCH_2C}H_2$ $(X = NH, O,:$



Electrophilic cleavage of $C - F$ bonds in $Pt(II) - CF_3$ complexes in the presence of diprotic O- and S-nucleophiles gives a series of dioxy- and dithio-carbenes.

$Pt(II)$-nitrile ligands give cycloaddition reactions with $^{-}O(CH_2)_nCl$ $(n = 2, 3)$ or $\overline{OCH_2C}H_2/Cl^-$ to yield 2-oxazolines and 1,3-oxazines:



n = 2, 3

A series of free oxazolines is obtained stoichiometrically using cationic $Pt(II)$ nitrile compounds; attempts to carry out these reactions under catalytic conditions are reported.

Highly reactive $Pt(0)$ carbene intermediates are involved in the reaction of $[(PPh_3)_2Pt(C_2H_4)]$ with $N_2CHCOOEt$, which affords, as the only isolated product, $[(PPh_3)_2Pt(trans - EtOOCCH = CHCOOEt)]$. By performing this reaction in the presence of styrene, the catalytic cyclopropanation of the olefin occurs. A mechanism based on the intermediacy of a $Pt(0)$-carbene is proposed on the basis of a $FAB - MS$ study.

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α-CHIRAL PLATINUM ALKYLS

P. BERGAMINI - E. COSTA - S. SOSTERO - O. TRAVERSO
P.G. PRINGLE - A.G. ORPEN

A new synthetic route to α-chiral platinum alkyls, recently developed by us[1] and other groups[2], is based on the insertion of a carbene deriving from a diazocompound into a Pt-halogen or a Pt-carbon bond.

$$[Pt] - L + N_2CHR \rightarrow [Pt] - CHRL + N_2$$

$[Pt] = Pt(II)$ complex
$L =$ Halogen, CH_3
$R = COOEt,\ COPh,\ COOMenth,\ SiMe_3$

The reaction of the sterically hindered $N_2CHSiMe_3$ with optically active platinum complexes $[PtX_2$ (chiral diphosphine)] $(X = Cl, Br, I)$ gives a pair of diastereomeric products $[PtX(CHXSiMe_3)$(chiral diphosphine)], one being largely predominant (up to 15:1 diastereomeric ratio) in some cases. For both the products $[PtBr(CHBrSiMe_3)(S, S$-chiraphos)] and $[PtCl(CHClSiMe_3)(S, S$-skewphos)], the major isomer has been separated in pure form and the absolute configuration at the α carbon has been determined by x-ray crystal structure.

The behaviour of the $PtCHXSiMe_3$ group (X=halogen) with respect to epimerization and halogen substitution has been explored.

These compounds are examples of α-chiral platinum alkyls with a single, assigned and stable configuration at the α carbon, which is a relevant character for the potential use of this class of compounds to investigate the mechanism of fundamental organometallic reactions and of asymmetric transformations catalysed by transition metals complexes.[3]

During this study, we observed that the group $Pt-CHXSiMe_3$ (X =halogen) can easily undergo desilylation in the presence of water, with loss of chirality:

$$[Pt]-CHXSiMe_3 \xrightarrow{H2O} [Pt]-CH_2X$$

This reaction can be used as a convenient alternative synthesis of chloromethylplatinum complexes avoiding the use of CH_2N_2.

When $N_2CHSiMe_3$ reacts with a substrate containing a $Pt-Me$ bond, both the chiral $PtCHMe-SiMe_3$ and the non chiral $Pt-CH_2SiMe_3$ groups can be formed, depending on the reaction conditions.

A mechanism for these transformations will be proposed on the basis of experimental observations.

REFERENCES

[1] P. Bergamini, E. Costa, S. Sostero, A.G. Orpen, P.G. Pringle *Organometallics 11*, (**1992**) 3879. P. Bergamini, E. Costa, S. Sostero, C. Ganther, J. Hogg, A.G. Orpen, P.G. Pringle *J. Organometallic Chemistry 455*, (**1993**) C13-C16 .

[2] R. McCrindle and A. McAlees, *Organometallics, 12*, **1993** 2445, .

[3] T.C. Flood, *Topics in Inorganic and Organometallic Stereochemistry*, Wiley, New York, 1981.

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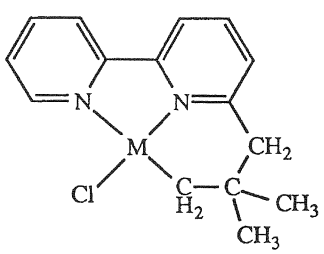
SYNTHESIS AND REACTIVITY OF CYCLOMETALLATED DERIVATIVES (d^8) WITH HETEROCYCLIC NITROGEN LIGANDS

G. MINGHETTI - M.A. CINELLU - S. STOCCORO - A. ZUCCA

Following our interest in the synthesis and reactivity of cyclometallated derivatives of d^8 metal ions with substituted pyridines and 2,2'-bipyridines[1], here we report new species arising from direct activation of alkyl C-H bonds.

The reaction of 6-(neopentyl)-2,2'-bipyridine, HL, with palladium(II) and platinum(II) intermediates, affords either adducts $(HL)MCl_2$ $(M = Pd)$ or cyclometallated species $(L)MCl$, 1, $(M = Pd, Pt)$ where L acts as an anionic terdentate ligand.



The new six-membered complexes, 1, will be compared with the five-membered species obtained from 6-(t-butyl)-2,2'-bipyridine.

From 1, $(M = Pt)$, a series of cationic mono and dinuclear species have been isolated by displacement of chloride with neutral mono or bidentate ligands, L^*, $[(L)Pt(L^*)]^+$ and $[(L)Pt - \mu(L^*) - Pt(L)]^{++}$.

In the case of palladium(II), under different conditions, a second type of metallated complexes can be obtained, which imply the "roll-over" of a pyridine ring.

The reactivity of the new metallated species with CO will be described and compared with that observed in metallated systems derived from benzyl-substituted ligands.

REFERENCES

[1] G. Minghetti, M.A. Cinellu, S. Stoccoro, A. Zucca, *Inorg Chem.*, **1990**, *29*, 5137; S. Stoccoro, G. Chelucci, M.A. Cinellu, A. Zucca, G. Minghetti, *J. Organomet. Chem., 450*, **1993**, C15, and references therein cited.

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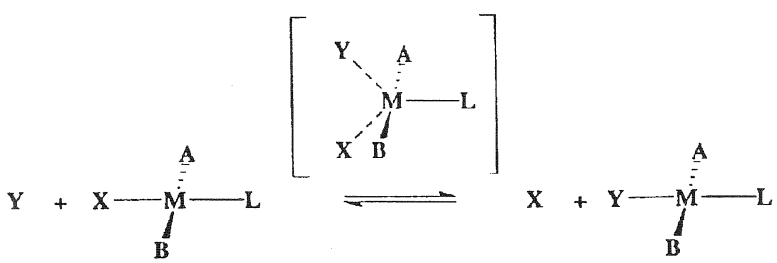
TRANS EFFECT IN PLATINUM(II) COMPLEXES AS MEASURED BY BUILT IN MOLECULAR GAUGES

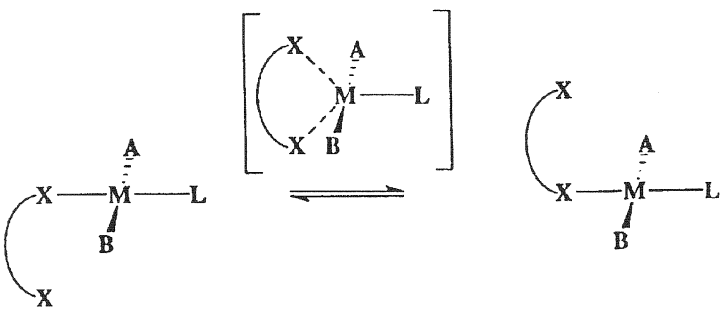
FRANCESCO PAOLO FANIZI - GIOVANNI NATILE

The task of compiling a reliable trans effect series, which could be useful for rationalizing and predicting inorganic reaction pathways, has involved more than one generation of inorganic chemists. In traditional substitution reactions (scheme 1), being the entering and leaving groups different, the effect of **L** on the reaction rate can be related either to the bond making or to the bond breaking depending upon which of the above processes is rate determining.



Scheme 1

As a consequence traditional trans effect series lack of general validity but depend upon the substitution reaction considered (i.e. the nature of **X** and **Y**). In order to overcome this problem, the entering and leaving ligand in the position trans to the ligand under test should be exactly the same. This condition has been recently used in a theorical work,[1] and can be accomplished by studying the intramolecular rate of exchange between the two ends of a monocoordinate symmetric bidentate ligand trans to the ligand whose trans effect is under test (scheme 2).[2]



Scheme 2

This dynamic process, can be investigated by variable temperature NMR spectroscopy. The exchange rate and $\Delta G^{\ddagger}$ can be easily obtained from line shape analysis of the spectra [for example for $\mathbf{M} = Pt$, $\mathbf{X} - \mathbf{X} = 2,9\text{-}Me_2 - 1,10\text{-phenanthroline}$, $\mathbf{A} = \mathbf{B} = PPh_3$, $\Delta G^{\ddagger}$ (kcal/mol) are: 10.4 (**L**=CI), 9.3 (**L**=Br), 7.8 (**L**=I)]. Moreover for such an intramolecular process the enthropic contribution is expected to be small. The steric and electronic properties of the bidentate ligand can be tuned in order the head to tail rearrangement to be measurable for ligands of very different trans effect. The effects of the total charge of the complex and of the cis ligands can also be investigated.

REFERENCES

[1] Z. Lin and M. B. Hall, *Inorg Chem, 30* **1991**, 646.

[2] F. P. Fanizzi, G. Natile, M. Lanfranchi, A. Tiripicchio, *lnorg., Chem,* **1994**, in press. F. P. Fanizzi, L. Maresca, G. Natile, M. Lanfranchi, A. Tiripicchio, G. Pacchioni, *J. Chem Soc, Chem Commun,* **1992**, 333.

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NUCLEOPHILIC REACTIVITY: DISSECTION INTO STERIC AND ELECTRONIC CONTRIBUTIONS

LUIGI MONSU' SCOLARO

The sequence of the n°_{Pt} values in the scale of nucleophilic reactivity constants reflects roughly the characteristics of softness of the d^8 metal center.[1] There are, however, several severe deviations due to the π acceptor properties of the ligands and/or to electrostatic interactions. An additional limit comes from the fact that for a donor atom no account is taken of a steric contribution to the reactivity, even though steric effects can strongly influence the values of the derived parameters. For instance, the n°_{Pt} values listed for Ph_3P, $n Bu_3P$ and Et_3P are almost identical (8.93, 8.96, and 8.99, respectively) and can lead to the wrong conclusion that phosphines are all strongly reactive regardless of the nature of the substituents on the phosphorous atom.

We decided to obtain quantitative informations on the relative importance of steric and electronic factors in determining the reactivity of phosphines and amines toward platinum(II). To this purpose a model complex $[PtPh_2(CO)L]$ (L=5-aminoquinoline or SEt_2), was particularly designed to favour an associative

substitution. In addition: **i)** the complex is uncharged and soluble in nonpolar solvents **ii)** only one group (5-Aq or SEt_2) undergoes the substitution process **iii)** the lability of the leaving group is not too high or too low **iv)** the changes in the electronic spectra occur in the near visible region **v)** one of the coordinated ligands, CO in this case, is a good probe of the changes of electronic density or of the steric repulsions induced by the entering ligand *Y* in the reaction products *cis*-$[PtPh_2(CO)(Y)]$.

The observed sequences of reactivity give the first extended scales of nucleophilic constants of phosphines[2] and amines[3] toward platinum(II). The values of the rate constants can be resolved quantitatively into electronic and steric effects, by means of correlations with the pKa values of the phosphines and amines or with some internal parameters of the system such as νCO, ^{1}J(PtP) or ^{1}J(PtCO) of the *cis*-$[PtPh_2(CO)(Y)]$ products. The electronic profiles of the reactions show that the reactivity is only slightly affected by σ-inductive effects brought about by substituents on the phosphorus or nitrogen atoms while steric effects are dominant. Different shapes of steric profiles for the two reactions were obtained by correlating the reactivity data with different sets of steric parameters such as the ligand cone angles (θ) of space-filling CPK molecular models or the van der Waals steric repulsion (Er) as derived from molecular mechanics calculations. Limits and significance of such relationships are discussed in order to account for apparently conflicting interpretations.

For the most sterically hindered amines, such as $NHCy_2$ or NEt_3, the bimolecular attack is prevented and the reaction proceeds only by way of a nucleophile independent pathway, which most likely involves dissociation of a ligand (5-Aq or SEt_2) from the coordination sphere of the metal. The same pathway controls the reaction with nitrogen bidentate ligands N-N, such as 2,2'-bipyridine or 1,10-phenanthroline, to yield $[PtPh_2(N\text{-}N)]$, where a fast ring closure follows the

displacement of 5-Aq or SEt_2. In contrast, in the reactions with 1,2-diaminoethane, 1,3-diaminopropane, 2-aminomethylpyridine, 2-aminoethylpyridine, 2,2'-dipyridylamine it is possible to observe by ^1H NMR the formation of an intermediate open-ring [$PtPh_2$(CO)N-N] species, which eventually interconverts slowly into the final [$PtPh_2$(N-N)] product. The proper kinetics were followed by IR or ^1H NMR spectroscopy. The contemporary presence in the starting substrate of a labile (SEt_2) and a relatively inert (CO) ligand allows for the isolation of some stable open ring species such as that obtained with N-phenyl-1,2-diaminoethane, where the two nitrogen atoms exhibit widely different basicity and steric hindrance. Preliminary results with hybrid bidentate ligands of the type P-N and P-S showed a fast entry of the phosphorus end of the molecule followed by a relatively slow ring closure.

REFERENCES

[1] (a) Belluco U.; Cattalini L.; Basolo F.; Pearson R. G.; Turco A., *J. Am. Chem. Soc.* **1965**, *87*, 241 (b) Pearson R. G.; Sobel H.; Songstad J., *J. Am. Chem. Soc.*, **1968**, *90*, 319.

[2] Romeo R.; Arena G.; Monsù Scolaro L., *Inorg. Chem.* **1992**, *31*, 4879.

[3] Romeo, R.; Arena G.; Monsù Scolaro L.; Plutino M. R.; Bruno G.; Nicolò F., *Inorg. Chem.* **1994**, in press.

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PERSPECTIVES IN SQUARE PLANAR SUBSTITUTION REACTIONS

L. CATTALINI

The general behaviour of platinum(II) complexes undergoing nucleophilic substitution of the coordinated ligands has been established since several years ago. The normal mechanism can be described as an asychronous associative substitution even if examples of dissociative mechanism are known. A sequence of reactivity has been established and more or less confirmed with a large number of substrates. A limited amount of data exist about the trans and cis kinetic effects and steric restrictions to substitution, and some case has been reported of "anchimeric assistence" and "electrophilic catalysis".

To predict new studies in this area is just a matter of phantasy. However, a number of points of interest are already clear.

A possibility exist to investigate more nucleophiles, on building up appropriate substrates and systems; mention can be made to oxygen donors (the nucleophilicity of hydroxide is still a matter of discussion), many sulphur donors, ion pairs and triplets, cationic donors, metal complexes acting as nucleophiles or producing electrophilic catalysis to nucleophilic substitution.

Synthetic aspects are obviously related to this subject.

Also the amount of data concerning different classes of leaving groups is limited and it may be of interest to investigate systems where strong donors such as phosphines and arsines undergo nucleophilic displacement. In a number of cases the problem seems to be more thermodynamic than kinetic, i.e. conditions have to be found to force the equilibria to the desired direction.

An open area is that concerning polynuclear complexes, from the study of bridge splitting reactions to that of the reactivity of bimetallic systems. Recent developments in the synthesis of new possible substrates (such as the "A-shaped" dimers) offer a number of possibilities. With an adequate instrumentation it may be of interest to apply the kinetic methods to investigate heterogeneous systems, such as those provided by resins containing the reactive substrates. Also the study of the role of an increasing steric hindrance on the reaction mechanism(s) would be of relevant interest.

Finally, a thema which can be developed is the use of kinetic tools to acquire more and precise knowledge of the chemicals bonds. An example will be presented.

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NON-ISOTHERMAL SPECTROPHOTOMETRIC KINETICS APPLIED TO INORGANIC REACTIONS

GIUSEPPE ALIBRANDI

A method based on non-isothermal analisys[1] has been used to obtain kinetic constants and activation parameters of some inorganic reactions in solution. The main feature of the method is to change the way of producing the kinetic data. Instead of obtaining single values of rate constants at single different temperatures, the aim is to produce in a single short experiment a $k(T)$ profile (i.e. a whole set of rate constants in a definite temperature range).

The reactions studied under various experimental conditions to test the method were the thermal decomposition of the alkyl solvento species *trans*-$[Pt(PEt_3)_2(n\text{-}C_4H_9)(CH_3OH)]^+$ to yield the *trans*-hydride $[Pt(PEt_3)_2(H)(CH_3OH)]^+$ in methanol[2] and the cis-trans isomerization of the cation $[Pt(PEt_3)_2(CH_3)(C_2H_5OH)]^+$ in ethanol.[3]

Experiments were carried out collecting by a computer the values of the absorbance of the reaction mixture while increasing the temperature in a linear way (Fig. 1). The absorbance-time

data collected were then processed by appropriate algorithms using both differential and integral methods to obtain the $k(T)$ profile (Fig. 2). In the integral method a direct best fitting to equation (1) was performed with D_0, D_∞, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ as the parameters to be optimized.

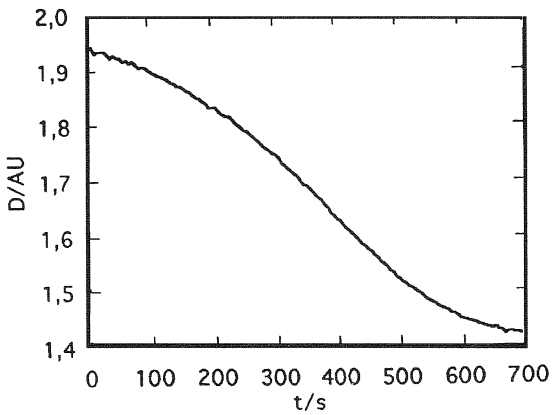

Figura 1

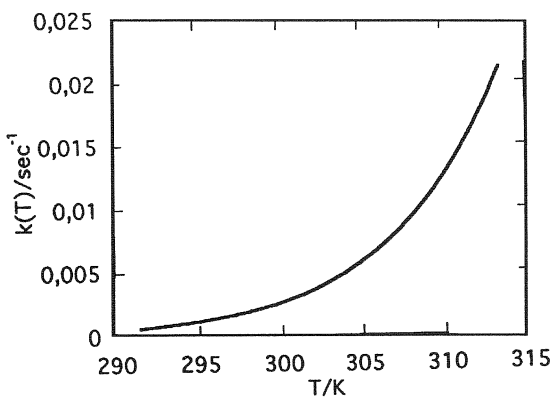

Figura 2

$$(1) \quad D_t = (D_0 - D_\infty e^{\left\{ -\frac{k}{h} e^{\left[\frac{\Delta S^{\neq}}{R}\right]} \int_0^t (T_0+\alpha t) e^{\left[-\frac{\Delta H^{\neq}}{R(T_0+\alpha t)}\right]} dr \right\}} + D_\infty$$

The activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ have very low statistical errors and are comparable with those obtained by the traditional isothermal method, where the error is greater.

For non-unimolecular reactions carried out under pseudo-first-order conditions (e.g. a nucleophilic substitution reaction on a square planar complex, where $k_{obs} = k_1 + k_2[Y]$) the $k(T)$ profile becomes a $k_{obs}(T)$ profile containing different contributions. In such cases it is necessary to perform the usual analysis of the dependence of k_{obs} on the concentration of all of the reagents that now can be made in the whole temperature range by a global fitting. A number of these cases are under investigation.

REFERENCES

[1] E. Koch, *Non-isothermal Reaction Analysis*, Academic Press, London, 1977 and References therein.

[2] R. Romeo, G. Alibrandi and L. Monsù Scolaro, *Inorg, Chem., 32* **(1993)** 4688.

[3] G. Alibrandi, D. Minniti, L. Monsù Scolaro and R. Romeo, *Inorg, Chem., 27* **(1988)** 318.

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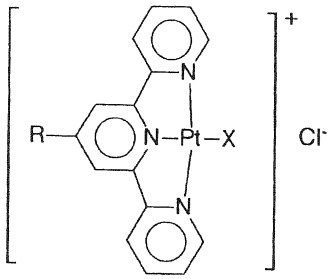
SYNTHESIS, CHARACTERIZATION ABSORPTION SPECTRA AND LUMINESCENCE PROPERTIES OF PLATINUM(II) TERPYRIDINE CATIONIC COMPLEXES

G. ARENA - G. CALOGERO G. - S. CAMPAGNA
L. MONSU' SCOLARO - V. RICEVUTO - R. ROMEO

A series of cationic complexes of platinum(II) containing terpyridine ligands of the type [Pt(R-terpy)X]Cl (R=H, Ph; X=Cl, Me, Ph) were synthesized and fully characterized by ^{1}H, ^{13}C and ^{195}Pt NMR spectroscopy. The terpyridine behaves as a tridentate ligand and no evidence of fluxionality has been found. ^{1}H NMR data are strongly indicative of a dimerization process in aqueous or alcoholic solution, as observed previously for other square planar compounds containing the same ligand [1] and in organometallic species with R=H and X=Me [2]. When X is a phenyl group the formation of the dimer is hindered.

The absorption spectra are dominated by intense bands in the UV region (ε in the range 10^4-10^5 $M^{-1}cm^{-1}$) attributed to terpy-centered (LC) transitions, and by moderately intense bands in the visible (ε in the range 10^3-10^4 M^{-1} cm^{-1}) assigned to metal-to-ligand charge transfer (MLCT) transitions.



All the compounds are strongly luminescent at 77K in MeOH/EtOH 4:1 (v/v) rigid matrices from LC and / or MLCT excited states (emission maxima in the range 500-600 nm, lifetimes on the microsecond time scale). Except for X=phenyl, the complexes exhibit a second luminescence band at lower energies, that can be attributed to a Pt-Pt σ^* to polypyridine ligand CT level. Most of the compounds are moderately luminescent in deoxygenated solutions even at room temperature. The emission bands are in all cases red-shifted with respect to the low temperature emission bands, confirming the charge transfer nature of the processes. The presence of the lower energy band supports the formation of dimeric species.

The structural and photophysical properties of these complexes are being investigated for their use as probes for nucleic acids.

REFERENCES

[1] Jennette K.W., Gill J.T., Sadownick J.A., Lippard S.J., *J. Am. Chem. Soc.* **1976**, *98*, 6159-6168. Lippard S.J., *Acc. Chem. Res.* **1978**, *11*, 211-217.

[2] manuscript in preparation.

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SYNTHESIS, CHARACTERIZATION AND DNA BINDING STUDIES OF A NOVEL PLATINUM(II) (2,2':6',2"-TERPYRIDINE) CATIONIC COMPLEX

G. ARENA - L. MONSU' SCOLARO
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A new organometallic cationic complex of platinum(II) containing 2,2':6',2"-terpyridine (terpy) ligand of the type [Pt(terpy)Me]X (X=Cl, NO_3, PF_6, ClO_4) was synthesized and characterized by ^1H, ^{13}C and ^{195}Pt NMR spectroscopy. There was no evidence of fluxionality for the terpyridine ligand that behaves as a terdentate while the fourth position in the coordination plane is blocked by the methyl group. Thus, resulting cationic complex is unreactive toward substitution under mild conditions. The high planarity of the terpy moiety is responsible for the occurrence of stacking interactions in aqueous solution with the formation of dimer or even higher oligomers. UV/VIS and ^1H NMR spectra show a characteristic dependence on the concentration of the complex, on the temperature, solvent and ionic strength. Analysis of the absorption spectra gives a value of 8800 M^{-1} for the dimerization equilibrium. The

interaction of the cationic complex with calf thymus DNA and two synthetic polynucleotides (Poly(dG-dC)$_2$ and Poly(dAdT)$_2$) was investigated by UV-VIS and CD spectroscopy. The value of the binding equilibrium constant of the complex with the double helix was estimated to be 10^5 M^{-1} by UV-VIS spectroscopy measurement. Gel electrophoresis on agarose of pUC19 and melting point measurements strongly support an intercalative mode of interaction.

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EQUILIBRIUM STUDIES OF α-DIIMINE DISPLACEMENT IN CATIONIC ALLYLPALLADIUM(II) COMPLEXES BY MONODENTATE N-DONOR LIGANDS AND THE MECHANISM OF ALLYL AMINATION BY TRIETHYLAMINE AND PYRIDINE

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In the cationic complexes $[Pd(\eta^3\text{-all})(N\text{-}N')]ClO_4$ (N-N′=1,2-bis(imino)ethanes or pyridine-2-carbaldimines) the chelated α-diimine is rapidly and reversibly displaced by secondary amines (N-methylaniline, morpholine, piperidine), triethylamine, and 4-substituted pyridines. The observed equilibrium constants K_e increase with increasing basicity and decreasing steric requirements of the entering N-donor ligand. They strongly depend on the α-diimine and decrease in the order RN=CH-CH=NR $\gg$ RN=C(Me)-C(Me)=NR = py-2-CH=NR (R=C_6H_4OMe-4). The complex $[Pd(\eta^3\text{-all})$ (py-2-CH=NC_6H_4OMe-4)]ClO_4 undergoes a slow allyl amination by triethylamine or pyridine (A) in the presence of fumaronitrile (fn), yielding $[Pd(\eta^2\text{-fn})$(py-2-CH=NC_6H_4OMe-4)] and Et_3N^+-$CH_2CH{=}CH_2$ or $C_5H_5N^+$-$CH_2CH{=}CH_2$. Kinetic studies show that the pseudo-first order rate constants of amination (k_{obs}) are given by $k_{obs}=k_2[A]$,

suggesting a direct bimolecular attack of A on the η^3-allyl ligand. The amination hardly proceeds in the presence of the less activated olefin dimethyl fumarate (dmf). The π-accepting properties of the olefinic ligands play an important role also in the oxidative addition of Et_3N^+-$CH_2CH{=}CH_2$ or $C_5H_5N^+$-$CH_2CH{=}CH_2$ to [Pd(η^2-ol) (py-2- $CH{=}NC_6H_40Me$-4)] (ol=fn, dmf), i.e. the reverse of the amination reaction.

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SYNTHESIS, STRUCTURE AND ANTITUMORAL ACTIVITY OF PLATINUM(II) COMPLEXES WITH AMIDRAZONE DERIVATIVES

M. T. COCCO - G. PONTICELLI

Platinum(II) complexes with amidrazone derivatives have been prepared and characterized by analytical and physical data, I. R. and electronic reflectance spectra.

These compounds have general formula $[Pt(L)_2X_2]$, where L=acetamidrazone, N^1-acetyl, 2-phenylacetamidrazone and N^1-ethoxycarbonyl-2-phenylacetamidrazone; X=CI or Br.

The complexes are powder-like, coloured yellow to brown, soluble in DMF and DMSO in which they do not conduct. These are trans square planar and the bases act as monodentate via a nitrogen of the acetamidrazone.

These compounds are tested in vitro with aid of Boehringer Mannheim Italia di Monza and Istituto Tumori di Milano towards L1210, A2780 and their sublines respect to cis-platin.

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CYCLOMETALLATED PLATINUM(II) AND PLATINUM(IV) COMPOUNDS WITH IMINIC LIGANDS

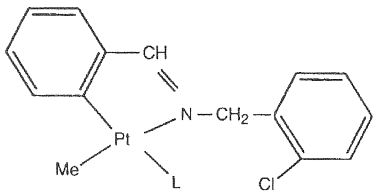
M. CRESPO - M. FONT-BARDÍA - X. SOLANS

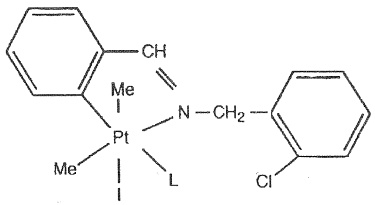
The chemistry of cyclometallated complexes has attracted much attention due to their utility in organic synthesis and catalysis. Moreover, interesting photochemical, photophysical and electrochemical properties have been reported recently for cyclometallated platinum compounds.

We wish to report the synthesis, characterization and reactivity of platinum cyclometallated compounds containing iminic ligands. The reaction of $[Pt_2Me_4(SMe_2)_2]$ with $C_6H_5CH{=}NCH_2C_6H_4Cl$ yields compound Ia by intramolecular $C-H$ bond activation followed by reductive elimination of methane.

Compound Ia reacts with PPh_3 to yield cyclometallated compound Ib, which has been characterized crystallographically. However, the reaction with bidentate ligand 1,2-bis(diphenylphosphino)ethane produces a $[C^-]$ unidentate system with cleavage of the metallocycle.

Upon oxidative addition of CH_3I, compounds Ia and Ib produce, respectively, cyclometallated platinum(IV) compounds IIa and IIb.





Ia L=SMe_2
Ib L=PPh_3

IIa L=SMe_2
IIb L=PPh_3

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STUDIES OF THE SOLVENT-EXCHANGE RATE OF $[Pt(CH_3CH_2CN)_4]\ (CF_3SO_3)_2$

OLA F. WENDT - LARS I. ELDING

Solvent-exchange of complexes of the type PtS_4^{2+} has been studied for S being e.g. H_2O[1], Me_2S[2], $DMSO$[3] and $MeNC$[4]. However, no N-bonded Pt-complex has so far been investigated, due to *inter alia* the instability of $Pt(MeCN)_4^{2+}$. Recently, the corresponding propionitrile complex has been synthesized[5] and we here present rate constants and activation parameters for the reaction

$$Pt(EtCN)_4^{2+} + 4EtCN - d5 \rightarrow Pt(EtCN - d5)_4^{2+} + 4EtCN$$

studied by $^1H - NMR$ and isotopic labeling. Unlike other solvent-exchange reactions of platinum(II) complexes studied so far there is a propionitrile indipendent contribution to the rate of the above reaction, corresponding to a solvent path. The k_1-and k_2-values at 30°C are $0.43 \cdot 10^{-4} s^{-1}$ and $2.4 \cdot 10^{-4}\ m^{-1}s^{-1}$. The activation entropies are -21 and -70 $J \cdot K^{-1} \cdot mol^{-1}$, respectively, indicating an associative mode of activation.

REFERENCES

[1] a) Groning O., Drakenberg T., Elding, L.I. *Inorg. Chem. 21* (**1982**), 1820

b) Helm L., Elding L.I., Merbach A.E., Inorg. Chem. *24* (**1985**), 1719

[2] Frey U., Elmroth S., Moullet B., Elding L.I., Merbach A.E., *Inorg. Chem. 30* (**1991**), 5033

[3] Ducommon Y., Helm L., Merbach A.E., Hellquist B., Elding L.I., *Inorg. Chem. 28* (**1989**), 377

[4] Hallinan N., Besançon, V., Forster M., Elbaze G., Ducommon Y., Merbach A. E., *Inorg. Chem. 30* (**1991**), 1112

[5] Kukuskin V.Y., Oskarsson A., Elding L.I., *Inorg. Synth.* accepted for publication, *31* (**1993**).

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TRIARYLPHOSPHINE Pt(II) COMPLEXES WITH AMINO ACIDS AND PEPTIDES

V. PAVONE - A. LOMBARDI - M. SAVIANO - O. MAGLIO

In recent years renewed attention has been addressed to the synthesis and physico-characterization of amino acids and peptides metal complexes.

Complexes of Pt(II), Co(III) and Cu(II) have been used in peptide synthesis and they can provide a significant contribution to peptide chemistry: N-terminal or C-terminal end protection during peptide synthesis.[1]

Platinum has been proven to be an effective amino protecting group of α-amino acids and its electron with-drawing properties seem to increase the reactivity of N-coordinated amino acid in the formation of peptide bond.[2]

Beside the studies of platinum(II) complexes containing two metal ion N-coordinated amino acid residues, in order to better evaluate the usefulness of these compounds in peptide synthesis, we undertook the synthesis and structural characterization of Pt(II) complexes containing a single N-coordinated α-mino acid.[3]

In this work we report the synthesis and solution characterization by NMR spectroscopy, of triarylphosphine Pt(II)

complexes with only one amino acidic residue. A detailed X-ray analysis is also reported.

REFERENCES

[1] W. Beck, *Pure and Appl. Chem., 60*, (**1988**), 1357.

[2] A. Lombardi, V. Pavone, C. Pedone, B. Di Blasio, E. Benedetti, *John Libbery Eurotext Ltd., Second Forum on Peptides, 174*, (**1989**), 207.

[3] A. Lombardi, O. Maglio, V. Pavone, B. Di Blasio, M. Saviano, F. Nastri, C. Pedone and E. Benedetti, *Inorg. Chim. Acta, 204*, (**1993**), 87.

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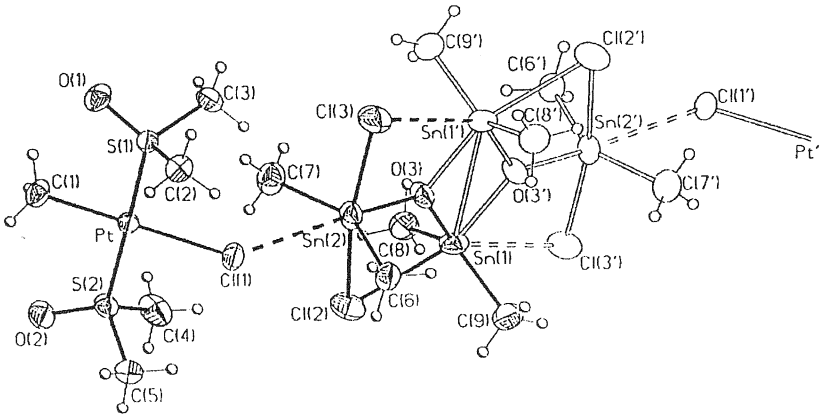
CRYSTAL AND MOLECULAR STRUCTURE OF *Trans*-CHLORO METHYL (bis-DIMETHYLSULFOXIDE) PLATINUM(II)

R. SCOPELLITI - F. NICOLÒ - G. BRUNO

Crystal data. $C_9H_{27}Cl_3O_3PtS_2Sn_2$, Triclinic, $M = 786.25$, space group $P\bar{1}$ (n° 2) with $a = 9.373(2)$ Å, $b = 9.5760(10)$ Å$c = 14.087(3)$ Å, $\alpha = 70.29(1)°$, $\beta = 72.50(1)°$, $\gamma = 72.21(2)$, V 1105.5(4) Å^3 $Z = 2$. Final $R = 0.0237$, $Rw = 0.0245$ $G.o.f = 1.085$ for 2505 independent reflections with $I \geq 3\sigma(I)$.

In the solid state the title complex co-crystallizes with the polinuclear tin(IV) compound: di-μ-3-oxo-bis(μ-dichloro)-bis(μ-dimethyl-tin(IV))-bis (chlorodimethyl-tin(IV)) [1]. This analysis is the first example of crystal structure of a *trans*-dimethyl sulfoxide platinum(II) compound [2]. The $Pt - S$ bond distances (mean value 2.259(2)Å) are slightly shorter than the value of 2.292(3)Åreported for the *trans*-dichlorobis(di-n-propyl sulfoxide) platinum(II) [3]. The long Pt-Cl bond distance of 2.416(2)Åis mainly due to both the strong*trans*-influence of the opposite methyl group and the interaction {3.442(2)Å} of Cl1 atom with the tin atom (Sn2).



REFERENCES

[1] P. H. Harrison, M. J. Begley and K. C. Molloy. *J. Org. Chem.*, **186** (1980) 213-236

[2] *Cambridge Structural Database* R. 5.06

[3] R. Melanson and F. D. Rochon. *Acta Cryst*(1988) **C44**, 1893-1895

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